REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY (*Leave Blank*)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	31 Dec 1997	Progress Report: 1 Oct 97 - 31 Dec 97

4. TITLE AND SUBTITLE
Nanocrystalline Processing and Interface Engineering of Nitrides

5. FUNDING NUMBERS
G - N00014-95-1-0626

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8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Office of Naval Research
800 North Quincy Street
Ballston Tower One
Arlington, VA 22217-5660

10. SPONSORING / MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION / AVAILABILITY STATEMENT
Approved for public release; distribution unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT (*Maximum 200 words*)
This report describes the preliminary results obtained in the study of a forced-flow reactor to synthesize nanocrystalline aluminum nitride. Variables such as starting material and the use of a nitriding plasma were examined. It was found that evaporating aluminum, rather than aluminum nitride, resulted in higher yields of material but with a higher level of unnitrided aluminum nanocrystals. The use of a microwave plasma is found to be critical to obtain high levels of nitridation. Future research includes post-nitridation of the nanocrystalline aluminum, and densification and evaluation of the nanocrystalline aluminum nitride.

14. SUBJECT TERMS	15. NUMBER OF PAGES
Nanocrystalline Processing, Aluminum Nitride	3
	16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	UL

"Nanocrystalline Processing and Interface Engineering of Si_3N_4-based Nanocomposites"

Technical Report on ONR Grant No. N00014-95-1-0626
for the period of October 1, 1997 - December 31, 1997

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Nanocrystalline Aluminum and Aluminum Nitride Synthesis

Based upon our previous success in synthesizing an easily densified nanocrystalline titanium nitride (TiN) powder [1], we have recently begun to extend this approach to the synthesis of nanocrystalline aluminum nitride (AlN) for electronic packaging applications. Aluminum nitride has some extremely useful properties such as high thermal conductivity, a coefficient of thermal expansion close to that of silicon, an extremely high electrical resistivity, and mechanical properties similar to those of alumina (Al_2O_3) (Table 1). The competing materials for thermal substrates applications are primarily beryllia (BeO), silicon carbide (SiC), and diamond. BeO is toxic in powder form and SiC has high dielectric losses, and diamond has thus far proven difficult to produce in fully dense bulk form, leaving AlN as perhaps the best alternative. The thermal conductivity of polycrystalline AlN, however, is generally significantly lower than the single crystal value due to the difficulty in sintering the pure material. Typically, several percent of oxide additives, such as Y_2O_3, are added to the AlN powders to produce a liquid phase at the sintering temperature in order to improve densification. However, the addition of the sintering aids results in a second phase which remains after cooling and reduces the thermal conductivity. In addition, the presence of oxygen, whether from the oxide sintering additives or present in the starting AlN powder, produces defects within the AlN grains further reducing the thermal conductivity of the sample. Therefore, to produce an optimal AlN material it is necessary to produce an AlN powder which is easily sinterable and has an extremely low oxygen content. These requirements are very similar to those achieved with our nanocrystalline TiN synthesis, although are perhaps even more stringent for AlN since oxygen contents as low as 0.8 mole percent and small differences in processing can reduce the thermal conductivity from over 300 $W\ m^{-1}\ K^{-1}$ to 100 $W\ m^{-1}\ K^{-1}$ [2]. In addition, AlN is susceptible to attack by moisture to form AlOOH which, if incorporated into the AlN, would result in high oxygen concentrations and low thermal conductivities. The atmospheric control during the processing of these nanocrystalline AlN powders therefore is extremely important.

Table 1. Comparison of various substrate material properties to that of silicon [3].

Property	AlN	Al_2O_3	BeO	SiC	Si
Physical					
Density (g/cm^3)	3.26	3.75	2.9	3.2	2.3
Young's Modulus (Mpsi)	48	49	47	57	24
Vickers Hardness (kg/mm^2)	1200	2500	1200	2000	
Bending Strength (kg/mm^2)	40	35	25	45	
Electrical					
Volume Resistivity (Ω·cm)	$>10^{14}$	$>10^{14}$	$>10^{14}$	$>10^{14}$	
Dielectric Constant (1 MHz)	8.5-8.7	9	6.7	40	
Dissipation Factor , $x10^{-4}$, 1 MHz	<14	3	3	500	
Dielectric Strength (kV/mm)	15	15	12	.07	
Thermal					
Thermal Conductivity (W/m·K)	160-250	25	260	270	150
TCE (ppm/°C) RT-100°C	2.65	7	6.5	3.7	2.3
RT-400°C	4.8	7.4	8	3.7	

Aluminum nitride powder synthesis thus far has been somewhat more challenging than TiN synthesis. We are examining several different parameters for the synthesis of AlN [4]. The first variable is feedstock, that is, the material which is melted or decomposed in the crucible to produce the nanocrystalline clusters that will undergo further nitridation. So far we have examined aluminum metal and aluminum nitride powder as starting materials. There are several drawbacks and benefits to using each material. Aluminum nitride is a very refractory material, but does decompose at temperatures above 2000°C and can therefore be used as a source for a stable flow of aluminum in the reactor. However, the decomposition rate is very low, resulting in low yields, and the AlN starting material typically has a higher oxygen content than desired. X-ray diffraction patterns of powders produced from aluminum nitride evaporation without and with the application of microwave plasma are shown in Figures 1(a) and (b) respectively. Aluminum is an obvious alternative starting material, however, we have found it difficult to control the evaporation rate due to the surface tension of the molten aluminum, and the molten aluminum tends to attack the graphite crucibles through the formation of aluminum carbide. These issues are being addressed through the application of coatings to the graphite crucibles and the use of different crucible materials. Despite these problems, we have successfully synthesized nanocrystalline aluminum and aluminum nitride using aluminum feedstock as shown in Figure 1(c). The average crystallite sizes for the mixed Al and AlN phases is 30 nm and 10-15 nm, respectively. The surface area of the powder is nearly 100 m^2/g. The materials produced from the evaporation of aluminum are typically a mixture of aluminum and AlN, with approximately 70-80 wt.% AlN. We believe that the residual aluminum metal is due to the rapid evaporation of the aluminum starting material and will disappear as we learn to better control the process. In general, these powders were synthesized under higher reactor pressures, 3-20 mbar, than those used to produce the optimum nanocrystalline TiN powder. We will be adjusting the reactor pressure to produce a smaller average crystallite size. The influence of the microwave on the degree of nitridation is quite impressive and is the second variable to be examined. Without the microwave plasma generating the nitrogen radicals, the material produced is essentially pure aluminum powder. This is illustrated by comparing Figures 1a) and b). Figure 1(a) is from a run in which AlN was decomposed into a stream of nitrogen

without the microwave plasma and produced pure aluminum. Figure 1(b) is the same feedstock of AlN but with the microwave operating at 600 W. Similarly, during the evaporation of pure aluminum without the microwave, only aluminum metal is recovered; while with the plasma operating at 600W, greater than 70 wt.% AlN is obtained (Figure 1(c)). Further experiments to improve the yield and quality of the AlN powder are underway.

Future experiments will investigate the nitridation kinetics of the as-prepared nanocrystalline metal to examine the effectiveness of post-nitridation on the nanocrystalline powder. In addition, powder handling procedures need to be established and densification experiments will be performed to examine and optimize the sinterability of the nanocrystalline AlN powders.

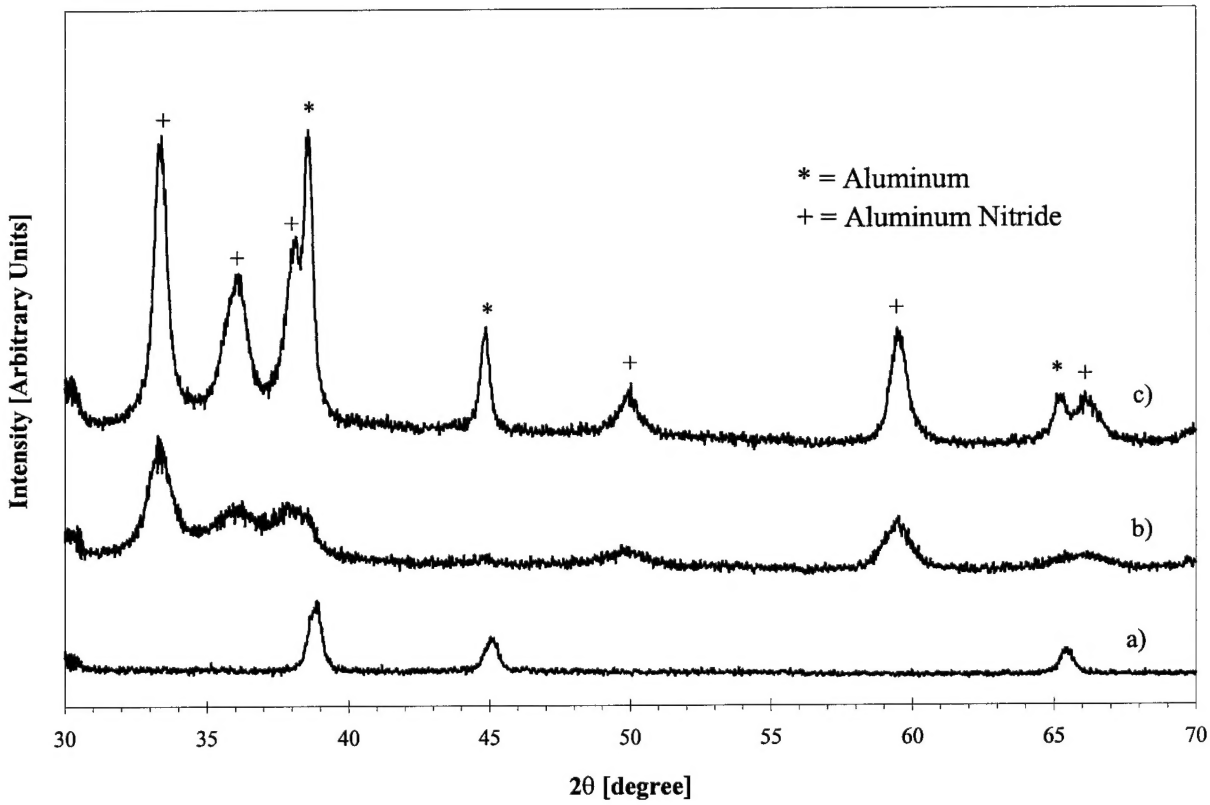

Figure 1. X-ray diffraction patterns of powders produced in tubular forced-flow reactor using (a,b) AlN and (c) Al as the starting material. Sample (a) was produced without the microwave plasma, whereas the samples in (b,c) were produced with the plasma operating at 600 W.

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